# Sum rules for inhomogeneous Coulomb systems

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Using the stationary equilibrium BBGKY hierarchy *and* some weak spatial decay properties of the correlations, we derive exact sum rules for the equilibrium distribution functions of ionic systems..Our results apply to both homogeneous and nonuniform systems. They show that *when* there is decay in such systems, *then* the total excess charge in the vicinity of a given number of fixed ions is zero, and that this excess charge has no dipole nor quadrupole moment. The implications for the static structure factor and for the dielectric tensor are discussed.

## I. INTRODUCTION

The rigorous statistical mechanical theory of large macroscopic formally infinite equilibrium systems with finite range or rapidly decaying interactions between the particles is based on the existence of infinite volume Gibbs states.[1] These are the generalization, via the Dobrushin, Lanford, and Ruelle equations, of the grand canonical ensemble for a system with a given temperature and fugacity in a finite box $\Lambda$, in $\nu$-dimensional space $\mathbf{R}^\nu$. They are also obtained (modulo some technical restrictions) as the infinite volume thermodynamic limit of all the different ensembles, e.g., microcanonical and canonical, used to describe finite systems in equilibrium.[2] It is very important in these considerations that the state, or probability distribution, in a given finite spatial region $\omega$ depends only on the configuration of particles in the vicinity of $\omega$. For strictly finite range interactions these are regions within a fixed distance of the boundary of $\omega$. Regions separated by a larger distance do not influence each other directly. Rapidly decaying potentials are then (loosely speaking) ones for which the influence of distant regions on the state in $\omega$ decreases sufficiently rapidly to make them unimportant. This requires at the *very least* that the potential be integrable at infinity, e.g., if the particles interact via a pair potential, then it should decay as fast as $r^{-(\nu+\epsilon)}$. This is the case for the type of potentials commonly used to model interactions between neutral atoms, e.g., the Lennard-Jones potential which decays as $r^{-6}$.

A problem occurs, however, when we are dealing with ionized systems in which the charges interact via the very long range Coulomb force (there may also be some problems for dipoles). In this case, there is no conceivable way in which distant parts of a system would be sufficiently decoupled for *arbitrary* configurations. The usual treatment of infinite volumes Gibbs states, e.g., the DLR equations,[2] will therefore not work here. We expect nevertheless that for *typical* configurations distant parts of an overall neutral system will sufficiently decouple, due to screening, to make the passage to the thermodynamic limit well defined. (For nonneutral systems the limit may present some extra problems.) More precisely, we expect the correlation functions to have well defined infinite volume limits. This has indeed been proven to be the case at sufficiently high temperatures and low densities, where the correlation functions were shown to cluster exponentially. The proof is based on the convergence of a cluster expansion especially adapted to this system.[3] The existence of the thermodynamic limit of correlation functions for "charge symmetric systems" has also been proven[4] based on correlation inequalities. These results, however, still leave open the question of how to characterize directly the infinite volume Gibbs states of general Coulomb systems in the absence of well defined DLR equations.

This question has been answered in an ingenious way for the one dimensional system,[5] where the electric field (at each point in space) was found to both describe the state of the system and to satisfy certain equilibrium equations. For higher dimensions the above method does not seem appropriate and a different characterization is necessary. One possibility is to use the Siegert or Sine–Gordon transform to new complex field variables for which one may perhaps be able to prove the existence of the thermodynamic limit and even some form of the DLR equations.[6]

In a recent series of papers[7–9] Gruber, Martin, and their associates have explored the consequences of assuming that the equilibrium correlation functions of Coulomb systems satisfy the stationary BBGKY (Bogolyubov, Born, Green, Kirkwood, and Yvon) hierarchy. These equations are obtained from the time dependent BBGKY hierarchy, which describes the time evolution of the $n$-particle spatial and momentum distribution functions of a classical system $f_n(x_1p_1, \ldots, x_np_n;\, t)$. These have the form[10,11]

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$$\partial f_n/\partial t = \mathcal{K}_n f_n + C_{n,n+1} f_{n+1}, \quad n=1,2,\ldots,$$

where $\mathcal{K}$ and $C$ are linear operators. Assuming that $f_n$ is a product of a Maxwellian momentum part and a purely spatial part and setting $\partial f_n/\partial t=0$ leads to an integro-differential equation for the $f_n$ [see Eqs. (1.1) and (1.2)]. These stationary equations are identically satisfied by the finite volume canonical and grand canonical distribution functions. It is also known that for short range potentials these equations are essentially equivalent to the DLR equations for the Gibbs states.[12] It is thus expected that the infinite volume limit of the correlations for charged systems will also satisfy them; in fact, this can be rigorously shown to hold for Coulomb systems in one dimension[5,7] and presumably it can also be established in all cases where the existence of the infinite volume limit has been proven.[3,4,6] It is therefore reasonable to expect that this is always true and explore the consequences which are nontrivial. In this paper, we extend the considerations of Refs. 7 and 8 to nonuniform systems and derive some new results also for homogeneous systems.

We consider a system consisting of $N$ species of charged particles with charges $z_\alpha$, $\alpha=1,2,\ldots,N$. These particles move either in the whole $\nu$-dimensional space $\mathbf{R}^\nu$ or in a restricted domain $\mathfrak{D}$ defined by appropriate walls. The only condition we impose on $\mathfrak{D}$ is that it extends to infinity in at least one direction. Typically, $\mathfrak{D}$ can be the half-space $\{x\in\mathbf{R}^\nu;\ x^1\geq 0\}$ of the electrode problem.

The particles interact by means of a two body force of the form $F^s_{\alpha_1\alpha_2}(x_1-x_2)+z_{\alpha_1}z_{\alpha_2}F(x_1-x_2)$, where $F^s_{\alpha_1\alpha_2}(x)$ is short range and $F(x)$ behaves like an inverse power law $|x|^{-\gamma}$ when $|x|\to\infty$ with some $\gamma\geq 0$. The case of main interest is of course the *Coulombic force* $F(x)\sim x/|x|^\nu$, $|x|\to\infty$, corresponding to the value $\gamma=\nu-1$. Another case of interest is the system of electrons with $F(x)\sim|x|^{-2}$ confined to a narrow layer above the surface of liquid helium,[13] which is often modeled as a two dimensional jellium corresponding to $\gamma=\nu$. It is thus instructive to consider general values of $\gamma$ in order to emphasize that the special properties of these systems are due to the long range nature of the forces for small values of $\gamma$.

It is only the long range part of the force which is relevant in our analysis, i.e., the results are independent of $F^s_{\alpha_1\alpha_2}(x)$. We shall therefore ignore $F^s$ from now on, pretending that $z_{\alpha_1}z_{\alpha_2}F(x)$ is the only force between the particles and taking $\nu-1\leq\gamma\leq\nu$. (We shall always keep the language of electrostatics speaking of the field due to the charged particles, and so on.)

The particles may also be subject to the action of various static external forces. We distinguish the following types:

(1) the electric field $D(x)$ due to a fixed distribution of charges external to $\mathfrak{D}$, e.g., the surface charges on the electrode plates;

(2) the field due to a uniform density of charge $\rho_B$ in $\mathfrak{D}$, systems with $\rho_B\neq 0$ are called jellium systems;

(3) the field due to a localized distribution of fixed charges $q(x)$ in $\mathfrak{D}$ [$q(x)$ may represent some external test charges in the system];

(4) an external force $F^w_\alpha(x)$ not of electrostatic nature; this may include the effects of the confining walls.

The thermodynamic equilibrium state of the system at a temperature $T$ is assumed to be described by means of correlation functions $\rho_{\alpha_1}(x_1)$, $\rho_{\alpha_1\alpha_2}(x_1,x_2)$, ..., which have their usual meaning, $\rho_{\alpha_1}(x_1)$ being the density of species $\alpha_1$ at $x_1$, etc. We shall often write these as $\rho(q_1)$, $\rho(q_1,q_2)$, ..., using the abbreviated notation $q_i=(\alpha_i,x_i)$. These functions are assumed to satisfy the stationary BBGKY equation given in the following form[10]:

$$k_BT\nabla_{x_1}\rho(q_1)=[F^w(q_1)+z_{\alpha_1}E(x_1)]\rho(q_1) + \int_{\mathfrak{D}} dy\sum_\alpha z_{\alpha_1}z_\alpha F(x_1-y)[\rho_{\alpha_1\alpha}(x,y)-\rho_\alpha(y)\rho_{\alpha_1}(x_1)]\,, \tag{1.1}$$

$$k_BT\nabla_{x_1}\rho(q_1q_2)=[F^w(q_1)+z_{\alpha_1}E(x_1)+z_{\alpha_1}z_{\alpha_2}F(x_1-x_2)]\rho(q_1q_2) + \int_{\mathfrak{D}} dy\sum_\alpha z_{\alpha_1}z_\alpha F(x_1-y) \times[\rho_{\alpha_1\alpha_2\alpha}(x_1x_2y)-\rho_\alpha(y)\rho_{\alpha_1\alpha_2}(x_1x_2)]\,. \tag{1.2}$$

Here $E(x)$ is the electric field due *to all the charges*, i.e., all the system's charges and all the external charges. It will therefore depend on the state of the system.

In order to understand Eqs. (1.1) and (1.2) and the structure of $E(x)$, it is useful to consider first the equilibrium distribution of finite systems in bounded regions $\{\Lambda\}$ and then take the thermodynamic limit $\Lambda\to\mathfrak{D}$. It is easily found that the correlation functions of the finite systems satisfy Eq. (1.1) with the electric field $E^\Lambda(x)$ given by

$$E^\Lambda(x)=D^\Lambda(x)+\int_\Lambda dyF(x-y)C^\Lambda(y)\,, \tag{1.3}$$

with

$$C^\Lambda(x)=\sum_\alpha z_\alpha\rho^\Lambda_\alpha(x)+q(x)+\rho_B \tag{1.4}$$

being the charge density at $x$. Let now $\Lambda\to\mathfrak{D}$ and assume that the state of the finite system converges to a state of the infinite system defined by Eqs. (1.1) and (1.2). We then have

$$E(x)=D(x)+\lim_{\Lambda\to\mathfrak{D}}\int_\Lambda dy\,F(x-y)C^\Lambda(y)\,,\qquad D(x)=\lim_{\Lambda\to\mathfrak{D}}D^\Lambda(x)\,. \tag{1.5}$$

It is convenient for the discussion of the equilibrium equations (1.1) and (1.2) to single out in $E(x)$ the contribution of the local charge density in $\mathfrak{D}$:

$$C(x)=\lim_{\Lambda\to\mathfrak{D}}C^\Lambda(x)=\sum_\alpha z_\alpha\rho_\alpha(x)+q(x)+\rho_B\,.$$

Writing

$$E(x)=G(x)+\lim_{\Lambda\to\mathfrak{D}}\int_\Lambda F(x-y)C(y)\,, \tag{1.6}$$

Eqs. (1.5) and (1.6) define the effective field $G(x)$:

$$G(x)=D(x)+\lim_{\Lambda\to\mathfrak{D}}\int_\Lambda dy F(x-y)[C^\Lambda(y)-C(y)] . \quad (1.7)$$

Clearly, the second term in Eq. (1.7) represents the field due to the system's charges located at infinity when $\Lambda$ becomes $\mathfrak{D}$. Therefore, one must remember that $G(x)$ has its origin both in external and in the system's charges which reside at "infinity" and are thus invisible in $C(x)$ for any fixed $x$.

An illustrative example showing how $G(x)$ is related to the polarization caused by boundary charges in simple geometries is given in Appendix A. It is these polarization effects which are responsible for the fact, already discussed in Refs. 7 and 8, that equilibrium states of infinite Coulomb systems can no longer be parametrized by purely external fields $D(x)$.

In the next sections, we shall study the physical implications that follow from various types of clustering conditions imposed on the equilibrium correlation functions. In all cases, we will assume that at least the following properties of integrable clustering hold:

$$\int dx_1 |\rho^T_{\alpha_1\alpha_2}(x_1,x_2)|<\infty , \quad (1.8)$$

$$\int dx_1 |\rho^T_{\alpha_1\alpha_2\alpha_3}(x_1,x_2,x_3)|<\infty , \quad (1.9)$$

$$\vdots$$

The truncated correlation function or Ursell functions are defined in the usual way:

$$\rho^T(q_1q_2)=\rho(q_1q_2)-\rho(q_1)\rho(q_2) , \quad (1.10)$$

$$\rho^T(q_1q_2q_3)=\rho(q_1q_2q_3)-\rho(q_3)\rho(q_1q_2) - \rho(q_1)\rho^T(q_2q_3)-\rho(q_2)\rho^T(q_1q_3) , \quad (1.11)$$

$$\vdots$$

To summarize, we take as the starting point of our analysis that the equilibrium state is described by correlation functions obeying Eqs. (1.1) and (1.2), with the clustering properties (1.8) and (1.9), and that $E(x)$ can always be written in the form (1.6) with some effective field $G(x)$.

## II. THE $l$-SUM RULES

The $l$-sum rules ($l=0,1,2$) are exact relations between the $n$ and the $(n+1)$ point correlation functions which will hold when *the rate of clustering of correlation functions is faster than the decrease of the force*. The simplest $l=0$ sum rule connecting the one and the two point functions is

$$z_{\alpha_1}\rho(q_1)+\int_{\mathfrak{D}} dx \sum_\alpha z_\alpha \rho^T(q_1q)=0 . \quad (2.1)$$

The $l=1$ and $l=2$ sum rules relate, respectively, the first and the second moment of the correlation functions:

$$z_{\alpha_1}x_1^i\rho(q_1)+\int_{\mathfrak{D}} dx \sum_\alpha z_\alpha x^i \rho^T(q_1q)=0 \quad (2.2)$$

and

$$d^i_{jk}(\hat{u})\left[z_{\alpha_1}x_1^jx_1^k\rho(q_1)+\int_{\mathfrak{D}} dx \sum_\alpha z_\alpha x^jx^k \rho^T(q_1q)\right]=0 \quad (2.3)$$

for $i=1,2,\ldots,\nu$, with summation on repeated indices. Here $\hat{u}$ is a unit vector pointing in any direction in which $\mathfrak{D}$ extends to infinity and $d^i_{jk}(\hat{u})$ is a tensor which characterizes the asymptotic behavior of the partial derivatives of the components $F^i(x)$ of the force at infinity; see Eq. (2.8).

These moment relations may be expressed as follows: Let $C(x|q_1)/\rho(q_1)$ be the *excess charge density* at $x$ when there is a particle of species $\alpha_1$ located at $x_1$:

$$C(x|q_1)=\sum_\alpha z_\alpha[\rho(q,q_1)+\rho(q_1)\delta_{\alpha\alpha_1}\delta(x-x_1)-\rho(q_1)\rho(q)] .$$

Then, for all $\alpha_1$ and $x_1$,

$$\int_{\mathfrak{D}} dx\, K_l(x)\, C(x|q_1)=0 , \quad l=0,1,2 , \quad (2.4)$$

with

$$K_0(x)=1, \quad K_1(x)=x , \quad K_2(x)=d_{jk}(\hat{u})x^jx^k .$$

$K_1$ and $K_2$ are $\nu$-component vectors.

The $l=0$ condition is well known for translation invariant states of Coulomb systems and has been used recently also for some semi-infinite systems.[14] It expresses the fact that the total amount of average charge in the atmosphere of the ion $\alpha_1$, located at $x_1$, exactly counterbalances that ion's own charge.[15] The sum rules (2.2) and (2.3) express the fact that the excess charge density carries no dipole or quadrupole moment.

These sum rules generalize in a natural way to the excess charge density

$$C(x|q_1,\ldots,q_n)=\sum_\alpha z_\alpha\Big[\rho(q,q_1,\ldots,q_n) +\sum_{j=1}^n \delta_{\alpha\alpha_j}\delta(x-x_j)\rho(q_1,\ldots,q_n)-\rho(q)\rho(q_1,\ldots,q_n)\Big],$$

where instead of keeping just one particle fixed at $x_1$ we keep $n$ particles fixed at $x_1,\ldots,x_n$. The sum rules then connect the $n+1$ and $n$ order correlation functions in the following way:

$$\left(\sum_{r=1}^n z_{\alpha_r}\right)\rho(Q)+\int_{\mathfrak{D}} dx\sum_\alpha z_\alpha[\rho(qQ)-\rho(q)\rho(Q)]=0 , \quad (2.1a)$$

$$\left(\sum_{r=1}^n z_{\alpha_r}x_r^i\right)\rho(Q)+\int_{\mathfrak{D}} dx\sum_\alpha z_\alpha x^i[\rho(qQ)-\rho(q)\rho(Q)]=0 , \quad (2.2a)$$

$$d^i_{jk}(\hat{u})\left\{\left(\sum_{r=1}^n z_{\alpha_r}x_r^jx_r^k\right)\rho(Q) +\int_{\mathfrak{D}} dx\sum_\alpha z_\alpha x^jx^k[\rho(qQ)-\rho(q)\rho(Q)]\right\}=0 , \quad (2.3a)$$

with

$$Q=(q_1,q_2,\ldots,q_n), \quad n=1,2,\ldots .$$

The full set of $l=0$ sum rules (also called canonical sum rules because they hold trivially in finite canonical ensembles) have been derived in Ref. 8 from the equilibrium equation for infinite systems ($\mathfrak{D}=\mathbf{R}^\nu$) without external charges.

Here we generalize the results of Ref. 8 in several respects. First, we derive the new set of sum rules

(2.2) and (2.3). Secondly, we show that the sum rules remain valid in the presence of external charges as well as for nonhomogeneous charged fluids. In particular, we consider general domains $\mathfrak{D}\subset \mathbf{R}^{\nu}$.

In the remainder of this section, we derive these sum rules from the BBGKY equation under suitable clustering assumptions. Some of their physical implications will be discussed in Sec. III. In order to keep the presentation as simple as possible, the details of the proofs are given in Appendix C.

### A. Conditions for sum rules

The sum rules follow from an asymptotic analysis of the second BBGKY equation as one of the points (say $x_1$) tends to infinity. For this analysis it is convenient to write the latter equation in terms of the truncated functions only. Using the definition [Eqs. (1.10) and (1.11)] and subtracting the first BBGKY equation from Eq. (1.2), we obtain

$$k_BT\nabla_{x_1}\rho^T(q_1q_2)=[F^w(q_1)+z_{\alpha_1}E(x_1)+z_{\alpha_1}z_{\alpha_2}F(x_1-x_2)]\rho^T(q_1q_2) \tag{2.5a}$$

$$+z_{\alpha_1}\rho(q_1)\left[z_{\alpha_2}\rho(q_2)F(x_1-x_2)+\int_{\mathfrak{D}}dx\sum_{\alpha}z_\alpha F(x_1-x)\rho^T(q_2q)\right] \tag{2.5b}$$

$$+z_{\alpha_1}\int_{\mathfrak{D}}dx\sum_{\alpha}z_\alpha F(x_1-x)\rho^T(q_1q_2q)\ . \tag{2.5c}$$

The basic assumption that the rate of clustering is faster than the decay of the force is expressed by the following conditions on the truncated functions (see note added in proof):

(C1):

$$\rho^T_{\alpha_1\alpha_2}(x_1,x_2)=O(1/|x_1|^{\nu+l+\epsilon})\quad(\epsilon>0)$$

as $x_1\to\infty$ in $\mathfrak{D}$, and

(C2):

$$\rho^T_{\alpha_1\alpha_2\alpha_3}(x_1,x_2,x_3)=O(1/|x_1|^{\nu+l+\epsilon})$$

as $x_1\to\infty$ in $\mathfrak{D}$, uniformly with respect to $x_2$.

In (C1) and (C2), homogeneity or periodicity of the state has not been assumed; we will only require that all species have nonvanishing average local densities as $x\to\infty$ in $\mathfrak{D}$ and that the effective field $E(x)$ as well as $F^w(q)$ are bounded at infinity in $\mathfrak{D}$:

(S1): there is a ball $B(x,r)$ of radius $r$ centered at $x$ such that

$$\int_{B(x,r)}dy\,\rho_\alpha(y)>\rho_0>0,\quad \text{as } x\to\infty \text{ in } \mathfrak{D};$$

(S2):

$$E(x)=0(1),\quad \text{as } x\to\infty \text{ in } \mathfrak{D},$$

$$F^w(q)=0(1)\ .$$

The two body forces for which the $l$-sum rules hold are characterized by the following properties:

(F1): $F(x)$ is locally integrable, and $l+1$ times differentiable at $x=\infty$;

(F2): $F(x)$ and its derivatives behaves for $|x|\to\infty$ as

$$\partial^{(m)}_{j_1\cdots j_m}F^i(\lambda\hat{x})=\frac{d^i_{j_1\cdots j_m}(\hat{x})}{\lambda^{\gamma+m}}+o\left(\frac{1}{\lambda^{\gamma+m}}\right),\quad 0\le m\le l,$$

$$\partial^{(l+1)}_{j_1\cdots j_{l+1}}F^i(x)=o(1/|x|^{\gamma+l})\ , \tag{2.6}$$

where $\hat{x}=x/|x|$ and the tensors $d^i_{j_1\cdots j_m}(\hat{x})$ are bounded functions of $\hat{x}$.

In the following we shall only consider asymptotically radial forces

$$F(x)\sim\hat{x}/|x|^{\gamma},\quad |x|\to\infty\ ,$$

so that

$$d^i(\hat{x})=\hat{x}^i\ ,$$

$$d^i_j(\hat{x})=\delta_{ij}-(\gamma+1)\hat{x}^i\hat{x}^j\ , \tag{2.7}$$

$$d^i_{jk}(\hat{x})=-(\gamma+1)[\delta_{ij}\hat{x}^k+\delta_{ik}\hat{x}^j+\delta_{jk}\hat{x}^i-(\gamma+3)\hat{x}^i\hat{x}^j\hat{x}^k]\ . \tag{2.8}$$

(Note, however, that asymptotic covariance under rotations is not essential in the derivation of the sum rules.)

### B. Derivation of the sum rules

We consider a fixed unit vector $\hat{u}$ in $\mathbf{R}^{\nu}$ such that $\mathfrak{D}$ contains the infinite half-cylinder $\{x_\lambda=\lambda\hat{u}+y;\ \lambda>0,\ |y|\le r\}$. We examine the asymptotic behavior of Eq. (2.5) as $x_1\to\infty$ in the following way: we set $x_1=x_\lambda=\lambda\hat{u}+y$, integrate both sides of Eq. (2.5) on a ball of radius $r$ centered around $\lambda\hat{u}$, and let $\lambda\to\infty$. *The main point is that the clustering assumptions* (C) *imply that the left-hand side of Eq* (2.5) *as well as the terms* (2.5a) *and Eq.* (2.5c) *are of order* $o(1/\lambda^{\gamma+l})$. *Therefore, we conclude from Eq.* (2.5) *that the term* (2.5b), *which is just the force at* $x_1$ *induced by an excess charge* $z_{\alpha_2}$ *at* $x_2$, *must also be* $o(1/\lambda^{\gamma+l})$, i.e.,

$$z_\alpha\int_{B(0,r)}dy\,\rho_{\alpha_1}(x_\lambda)\left[z_{\alpha_2}F(x_\lambda-x_2)\rho(q_2)+\int_{\mathfrak{D}}dx\sum_\alpha z_\alpha F(x_\lambda-x)\rho^T(q_2q)\right]$$

$$=z_\alpha\int_{B(0,r)}dy\,\rho_{\alpha_1}(x_\lambda)\left[\int_{\mathfrak{D}}dxF(x_\lambda-x)C(x|q_2)\right]=o\left(\frac{1}{\lambda^{\gamma+l}}\right) \tag{2.9}$$

(see lemma 2 in Appendix C).

### C. $l=0$ sum rule

Assume that the clustering hypotheses are true with $l=0$. It follows then from (F2) (see also lemma 1 in Appendix C) that taking the limit $\lambda\to\infty$ in Eq. (2.9) yields

$$z_{\alpha_1}\hat{u}^i \int_{B(0,r)} dy\, \rho_{\alpha_1}(x_\lambda)\left[z_{\alpha_2}\rho(q_2)+\int_{\mathfrak{D}} dx \sum_\alpha z_\alpha \rho^T(q_2,q)\right]=0 \ . \tag{2.12}$$

The $l=0$ sum rule (2.1) is then established by using the nonvanishing density condition (S1).

### D. $l=1$ sum rule

Assume that the clustering hypotheses are true for $l=1$. We can now use the $l=0$ sum rule (2.1) to subtract $F(x_\lambda)$ from $F(x_\lambda - x)$ in Eq. (2.9) to obtain

$$z_{\alpha_1}\int_{B(0,r)} dy\,\rho_{\alpha_1}(x_\lambda)\left\{\int_{\mathfrak{D}} dx[F(x_\lambda-x)-F(x_\lambda)]\,C(x|q_2)\right\}=O\left(\frac{1}{\lambda^{\gamma+1}}\right) \ . \tag{2.10}$$

Now letting $\lambda\to\infty$, we get (see lemma 1, Appendix C)

$$d^i_j(\hat{u})\left[z_{\alpha_2}x^j_2\rho(q_2)+\int_{\mathfrak{D}} dx \sum_\alpha z_\alpha x^j\rho^T(q_2 q)\right]=0 \tag{2.11}$$

for $i=1,\ \ldots,\ \nu$. When the matrix $d^i_j(\hat{u})$ [Eq. (2.7)] is invertible, and $\det[d^i_j(u)]=-\gamma\neq 0$, the $l=1$ sum rule (2.2) follows from Eq. (2.11). This is true in all cases, with the exception of the one dimensional Coulomb system for which $\gamma=\nu-1=0$.

### E. $l=2$ sum rule

Assume that the clustering hypotheses are true for $l=2$. We now use Eqs. (2.1) and (2.2) to subtract in Eq. (2.9) the two first terms of the asymptotic development of the force

$$z_{\alpha 1}\int_{B(0,r)} dy\,\rho_{\alpha_1}(x_\lambda)\left[\int_{\mathfrak{D}} dx[F(x_\lambda-x)-F(x_\lambda)+x^j(\partial_j F)(x_\lambda)]\,C(x|q_2)\right]=o(1/\lambda^{\gamma+2}) \ . \tag{2.12}$$

The $l=2$ sum rule (2.3) then follows again (except for one dimensional Coulomb systems) by taking the $\lambda\to\infty$ limit.

### F. Remarks

(a) To reduce the $l=1$ and $l=2$ sum rules from the above analysis it is necessary that $\gamma\neq 0$, i.e., that the force tends to zero at infinity. As already noted, these sum rules cannot be derived for one dimensional Coulomb systems. In fact, the $l=1$ sum rule does not hold for the periodic states of the one dimensional Coulomb jellium. Indeed, it is shown[16,17] that for this particular system

$$k_B T\frac{d}{dx}\rho(x)=2\rho_B\left\{x\rho(x)+\int_{-\infty}^{\infty} dy\, y[\rho(x,y)-\rho(x)\rho(y)]\right\}\neq 0 \ .$$

In all cases, the implications of the $l=2$ sum rule depends on the specific structure of the tensor $d^i_{jk}(\hat{u})$. This will be studied in the next section.

(b) For translation and rotation (Euclidian) invariant states Eqs. (2.1) and (2.2) are equivalent and also equivalent to Eq. (2.3) when $\gamma=\nu-1$. Indeed, if one replaces $x_1$ by $x_1+a$ in Eq. (2.2) and uses the translation invariance, one obtains

$$z_{\alpha_1}(x_1+a)\rho_{\alpha_1}+\int dx(x+a)\sum_\alpha z_\alpha \rho^T_{\alpha_1\alpha}(x_1 x)=0 \ .$$

Since $a$ is arbitrary, Eq. (2.1) follows.

Conversely, inserting Eq. (2.1) in Eq. (2.2), we find

$$\begin{aligned} &z_{\alpha_1}x_1\rho_{\alpha_1}(x_1)+\int dx\sum_\alpha z_\alpha x\rho^T(q_1 q)\\ &=\int dx(x-x_1)\sum_\alpha z_\alpha\rho^T(q_1 q)=\int dx\sum_\alpha z_\alpha x\rho^T_{\alpha_1\alpha}(|x|,0) \ .\end{aligned} \tag{2.13}$$

The invariance of $\rho^T(q_1 q)$ under rotations implies that the right-hand side of Eq. (2.13) vanishes. Moreover, if Eqs. (2.1) and (2.2) hold, one can use the Euclidian invariance to obtain

$$\begin{aligned} d^i_{jk}(\hat{u})\left[z_{\alpha_1}x^j_1 x^k_1\rho(q_1)+\int dx\sum_\alpha z_\alpha x^j x^k\rho^T(q_1 q)\right]&=d^i_{jk}(\hat{u})\int dx\sum_\alpha z_\alpha x^j x^k \rho^T_{\alpha,\alpha_1}(|x|,0)\\ &=\left[\frac{1}{\nu}\int dx\sum_\alpha z_\alpha|x|^2\rho^T_{\alpha,\alpha_1}(|x|,0)\right]\left[\sum_k d^i_{kk}(\hat{u})\right]=0\end{aligned}$$

since, by Eq. (2.8), $\sum_k d^i_{kk}(\hat{u})=-(\gamma+1)\hat{u}^i(\nu-1-\gamma)=0$ for $\gamma=\nu-1$.

## III. THE STATIC STRUCTURE FACTOR IN NONHOMOGENEOUS CHARGED FLUIDS

We discuss here the implications of the $l$-sum rules on the static structure factor. Other consequences of the sum rules were derived in Refs. 8 and 9.

Much information of interest regarding the equilibrium properties of fluids of charged particles, e.g., electrolytes, can be derived from the structure factor $S_x(k)$, the Fourier transform of the truncated charge–charge correlation function:

$$S_x(k)=\int_{\mathfrak{D}} dy\, e^{ik(x,y)} S(x,y) ,$$
$$S(x,y)=\langle Q_x Q_y\rangle - \langle Q_x\rangle\langle Q_y\rangle , \qquad (3.1)$$
$$Q_x=\sum_j z_{\alpha_j}\delta(x-x_j) .$$

In terms of the particle-correlation functions,

$$S(x,y)=\delta(x-y)\sum_\alpha z_\alpha^2\rho_\alpha(x)+\sum_{\alpha\beta} z_\alpha z_\beta \rho^T_{\alpha\beta}(x,y)$$
$$=\sum_\alpha z_\alpha C(x|y,\alpha) . \qquad (3.2)$$

If the fluid is nonhomogeneous, we can consider together with $S_x(k)$ its spatial average $\bar{S}(k)$:

$$\bar{S}(k)=\lim_{v\to\mathfrak{D}}\frac{1}{|V|}\int_V dx\, S_x(k) . \qquad (3.3)$$

The behavior of $S_x(k)$ as $k\to 0$ is given by the first terms of its Taylor expansion

$$S_x(k)=S_x(0)+\sum_{j=1}^{\nu} k^j\left(\frac{\partial}{\partial k^j}S_x\right)(0) + \sum_{i,j=1}^{\nu} k^i k^j \eta^{ij}(x)+o(|k|^2) , \qquad (3.4)$$

with

$$S_x(0)=\int_{\mathfrak{D}} dy\, S(x,y) , \qquad (3.5)$$

$$\left(\frac{\partial}{\partial k^j}S_x\right)(0)=i\int_{\mathfrak{D}} dy\,(x-y)^j S(x,y) , \qquad (3.6)$$

$$\eta^{ij}(x)=-\frac{1}{2}\int_{\mathfrak{D}} dy\,(x-y)^i(x-y)^j S(x,y) . \qquad (3.7)$$

For a translation and rotation invariant state, one has $S(x,y)=\bar{S}(|x-y|)$ so that

$$S_x(k)=\bar{S}(k)=\bar{S}(0)+\eta|k|^2+o(|k|^2) , \qquad (3.8)$$

with

$$\eta=\frac{1}{2\nu}\int dx\,|x|^2\bar{S}(|x|) .$$

It is generally assumed that *Coulomb systems* satisfy the shielding property expressed by the condition that the inverse of the static dielectric function $\epsilon(k)$ vanishes as $|k|\to 0$:

$$\epsilon^{-1}(k)=1-\left(\frac{1}{k_BT}\right)\frac{\omega_\nu}{|k|^2}S(k)\to 0, \quad |k|\to 0 , \qquad (3.9)$$

with

$$\omega_1=2, \quad \omega_2=2\pi, \quad \omega_3=4\pi .$$

This can be verified explicitly in the domain where the cluster expansion is valid[3] and follows also from some very reasonable assumptions on the "direct correlation function."[18] Equation (3.9) then yields

$$\bar{S}(k)=(k_BT)\,\frac{|k|^2}{\omega_\nu}+o(|k|^2) , \qquad (3.10)$$

$$\bar{S}(0)=0 , \qquad (3.11)$$

$$\eta=\frac{k_BT}{\omega_\nu}=-\frac{1}{2\nu}\int dx\,|x|^2\sum_{\alpha\beta} z_\alpha z_\beta\rho^T_{\alpha\beta}(|x|,0) . \qquad (3.12)$$

Equations (3.11) and (3.12) were derived under those conditions[15] and are known as the two Stillinger–Lovett moment conditions.

Clearly, the $l=0,1$ moment conditions imply that the first two terms on the right side of Eq. (3.4) vanish also for nonhomogeneous systems. To determine the quadratic term in Eq. (3.4), we combine Eqs. (2.1)–(2.3) to get

$$d^i_{jk}(\hat{u})\int_{\mathfrak{D}} dy\,(x-y)^j(x-y)^k\sum_\beta z_\beta\rho^T_{\alpha\beta}(x,y)=0 . \qquad (3.13)$$

Solving Eq. (3.13) for an asymptotically radial force with $d^i_{jk}(\hat{u})$ given by Eq. (2.8), we note that

$$\hat{u}_i\, d^i_{jk}(\hat{u})=(\gamma+1)[(\gamma+1)\hat{u}_j\hat{u}_k-\delta_{jk}]$$

and for any unit vector $\hat{v}$ orthogonal to $\hat{u}$

$$\hat{v}_i\, d^i_{jk}(\hat{u})=-(\gamma+1)(\hat{v}_j\hat{u}_k+\hat{v}_k\hat{u}_j) .$$

Therefore, Eq. (3.13) implies

$$(\gamma+1)\int_{\mathfrak{D}} dy\,|(x-y)\cdot\hat{u}|^2\sum_\beta z_\beta\rho^T_{\alpha\beta}(x,y)$$
$$=\int_{\mathfrak{D}} dy\,|x-y|^2\sum_\beta z_\beta\rho^T_{\alpha\beta}(x,y) \qquad (3.14)$$

and

$$\int_{\mathfrak{D}} dy[(x-y)\cdot\hat{u}][(x-y)\cdot\hat{v}]\sum_\beta z_\beta\rho^T_{\alpha\beta}(x,y)=0 \qquad (3.15)$$

for any $\hat{v}$ orthogonal to $\hat{u}$.

It is not difficult to check that if Eqs. (3.14) and (3.15) are true for two linearly independent unit vectors $\hat{u}_1$ and $\hat{u}_2$, they remain valid for all the unit vectors in the plane spanned by $\hat{u}_1$ and $\hat{u}_2$.

If $\mathfrak{D}$ contains an open cone, there is a choice of $\nu$ linearly independent vectors $\hat{u}_r$, $r=1,\ldots,\nu$, for which Eqs. (3.14) and (3.15) hold, and we can therefore conclude that

$$\int_{\mathfrak{D}} dy\cdot(x-y)^i(x-y)^j\sum_\beta z_\beta\rho^T_{\alpha\beta}(x,y)$$
$$=\begin{cases}-2\delta_{ij}\eta_\alpha(x), & \gamma=\nu-1(\neq 0) ,\\ 0, & \gamma\neq\nu-1 ,\end{cases}$$

with

$$\eta_\alpha(x)=-\frac{1}{2\nu}\int_{\mathfrak{D}} dy\,|x-y|^2\sum_\beta z_\beta\rho^T_{\alpha\beta}(x,y) .$$

This, together with Eq. (3.2), implies that the tensor (3.7) of the second derivative of $S_x(k)$ is isotropic:

$$\eta^{ij}(x) = \begin{cases} \delta_{ij} \sum_\alpha \eta_\alpha(x) = \delta_{ij}\eta(x), & \gamma = \nu - 1 (\neq 0) , \\ 0 , & \gamma \neq \nu - 1 . \end{cases} \tag{3.16}$$

We see that as a consequence of the sum rules the structure factor, even in a nonhomogeneous situation, must behave as

$$S_x(k) = \eta(x) |k|^2 + o(|k|^2) ,$$
$$\bar{S}(k) = \eta |k|^2 + o(|k|^2) , \tag{3.17}$$

with

$$\eta = \lim_{v \to \mathfrak{D}} \frac{1}{|V|} \int_V \eta(x) dx .$$

We have, however, been unable, so far, to derive Eq. (3.12) using only the clustering assumptions leading to the sum rules.

### A. Dielectric tensor

Another consequence of the $l = 2$ sum rule is that the bulk contribution to the dielectric tensor has to be isotropic even in a nonuniform Coulomb system. For a finite system in $\Lambda$, the static dielectric tensor is defined as

$$\epsilon_{ij}^{-1(\Lambda)} = \partial E_i^{(\Lambda)} / \partial D_j = \delta_{ij} - \omega_\nu \eta_{ij}^{(\Lambda)} .$$

$\eta_{ij}^{(\Lambda)} = \partial P^{i(\Lambda)} / \partial D_j$ is the response of the average polarization to a constant applied field $D$:

$$\eta_{ij}^{(\Lambda)} = \frac{1}{k_B T} \frac{1}{|\Lambda|} \int_\Lambda dx \int_\Lambda dy\, x^i x^j S^{(\Lambda)}(x, y) .$$

Using the canonical sum rule $\int_\Lambda dy\, S^{(\Lambda)}(x,y) = 0$ (which is always true in a finite canonical ensemble), $\eta_{ij}^{(\Lambda)}$ can be equivalently written as

$$\eta_{ij}^{(\Lambda)} = -\frac{1}{2k_B T} \frac{1}{|\Lambda|} \int_\Lambda dx \int_\Lambda dy (x-y)^i (x-y)^j S^{(\Lambda)}(x,y) . \tag{3.18}$$

The bulk contribution to $\epsilon_{ij}$ is obtained by replacing $S^{(\Lambda)}(x,y)$ in Eq. (3.18) by its infinite volume limit $S(x,y) = \lim_{\Lambda \to \mathfrak{D}} S^{(\Lambda)}(x,y)$:

$$\epsilon_{ij}^{-1(\text{bulk})} = \delta_{ij} + \frac{\omega_\nu}{2k_B T} \lim_{\Lambda \to \mathfrak{D}} \frac{1}{|\Lambda|} \int_\Lambda dx \int_{\mathfrak{D}} dy (x-y)^i (x-y)^j S(x,y) . \tag{3.19}$$

Comparison with Eqs. (3.16) and (3.17) gives

$$\epsilon_{ij}^{-1(\text{bulk})} = \delta_{ij} [1 - (\omega_\nu / k_B T) \eta] . \tag{3.20}$$

Thus, $\epsilon_{ij}^{(\text{bulk})}$ is isotropic and Eq. (3.20) gives the interpretation of the coefficient $\eta$.

### B. Remarks

(a) In the present derivation of the small $k$ behavior (3.17) of the structure factor, no *a priori* assumptions on the direct correlation function or on the dielectric function have been made. The result depends only on the validity of the sum rules. As established in the previous section, the latter follows from the equilibrium equations and the clustering properties of the state.

(b) In the case of the Coulomb force, the $l = 2$ sum rule does not fix the value of $\eta$. If the condition $\epsilon_{ij}^{-1(\text{bulk})} = 0$ is fulfilled, one finds again from Eq. (3.20) that $\eta = k_B T / \omega_\nu$, generalizing the second Stillinger–Lovett moment condition to nonhomogeneous fluids.

(c) Since we find $\eta = 0$ if the force is different from Coulomb and if the clustering with $l = 2$ holds, one sees that the second moment condition (3.12) is valid only for Coulomb systems, as has been conjectured.[15] We expect that for forces decreasing faster than Coulomb, the $l = 2$ sum rule is not valid.

## IV. "COMPLETE SHIELDING"

We now discuss the shielding of a localized distribution of external arbitrary fixed charges $q^*(x)$ in an equilibrium state; the introduction of such charges in the system (everything else remaining the same) will induce a modification of the charge density which is expected, at least in $\nu \geq 3$, to screen completely the fixed charges. Let $\rho_\alpha^*(x)$ and $\rho_\alpha(x)$ be the particle densities of the same state in the presence and in the absence of the distribution $q^*(x)$, respectively.

The "complete shielding" property is

$$\int_{\mathfrak{D}} dx \left\{ \sum_\alpha z_\alpha [\rho_\alpha^*(x) - \rho_\alpha(x)] \right\} + \int_{\mathfrak{D}} dx\, q^*(x) = 0 . \tag{4.1}$$

In the particular case where $q^*(x)$ is a distribution of point particles of the same species as those which constitute the system itself, i.e.,

$$q^*(x) = \sum_{i=1}^n z_{\alpha_i} \delta(x - x_i) ,$$

then the $n$th order canonical sum rule $l = 0$ implies complete shielding. Indeed, in this case

$$\rho_\alpha^*(x) = \rho(x, \alpha, q_1, \ldots, q_n) / \rho(q_1, \ldots, q_n) \tag{4.2}$$

and Eq. (4.1) becomes identical with Eq. (2.1a).

The situation is very different, however, for the case when the external charges are not integer multiples of the $z_\alpha$. It is easy to see that such charges cannot be shielded in one dimension while it follows from the cluster expansion[3] that they are shielded at high enough temperatures in two and three dimensions. It was shown recently by Fröhlich and Spencer[19] that this shielding disappears at low temperatures for the two dimensional system (at least for lattice systems with charge symmetry). This is due to the condensation of charges into dipoles and the result is as beautiful as the proof is complicated; the situation in three dimensions is far from certain. Our discussion here is therefore speculative. Consider states for which the field $G$ in the absence of $q^*$ can be taken constant throughout the whole domain $\mathfrak{D}$. Typical examples are infinite volume states in $\mathbf{R}^\nu$ or in a half-space $\mathbf{R}_+^\nu$ obtained as the thermodynamic limit of finite volume systems confined between two plane electrodes (see Apppendix A). The correlation functions $\rho^*(q)$ and $\rho^*(q_1 q_2)$ of such systems in the presence of the external charges $q^*(x)$ obey the first BBGKY equation (1.1) with

$$E^*(x) = G^* + \int_{\mathfrak{D}} dy\, F(x-y)C^*(y) ,$$

$$C^*(y) = \sum_\alpha z_\alpha \rho^*_\alpha(y) + \rho_B + q^*(y) . \qquad (4.3)$$

The correlations $\rho(q)$ and $\rho(q_1 q_2)$ of the same system without the external charges obey Eq. (1.1) with $q(x)=0$ in Eq. (1.4).

We now show that complete shielding occurs (except in one dimensional Coulomb systems) under certain assumptions on the modification at infinity induced by the fixed charges. Precisely, we assume

(i) the force is as in conditions (F1) and (F2), with $\gamma > 0$ and $l = 0$,

(ii) $\rho^*_\alpha(x) - \rho_\alpha(x) = O(1/|x|^{\nu+\epsilon})$ $(\epsilon > 0)$ ,

(iii) $\rho^{*T}_{\alpha_1\alpha_2}(x_1, x_2) - \rho^T_{\alpha_1\alpha_2}(x_1, x_2) = O(1/|x_1|^{\nu+\epsilon})$ ,

uniformly with respect to $x_2$ in $\mathfrak{D}$.

To establish the shielding property, we write the BBGKY equation (1.1) for the difference between the perturbed and the unperturbed state:

$$k_B T \nabla_{x_1}[\rho^*_{\alpha_1}(x_1) - \rho_{\alpha_1}(x_1)]$$
$$= [F^w(q_1) + z_{\alpha_1} E^*(x_1)][\rho^*_{\alpha_1}(x_1) - \rho_{\alpha_1}(x_1)] \qquad (4.4a)$$
$$+ z_{\alpha_1}[E^*(x_1) - E(x_1)]\rho_{\alpha_1}(x_1) \qquad (4.4b)$$
$$+ \int_{\mathfrak{D}} dx_2 \sum_{\alpha_2} z_{\alpha_1} z_{\alpha_2} F(x_1 - x_2)[\rho^{*T}_{\alpha_1\alpha_2}(x_1, x_2) - \rho^T_{\alpha_1\alpha_2}(x_1, x_2)]. \qquad (4.4c)$$

One can then proceed exactly in the same way as in the derivation of the sum rules. One sets $x_1 = \lambda\hat{u} + y$, integrates both sides of Eq. (4.4) on a ball of radius $r$ centered around $\lambda\hat{u}$, and let $\lambda \to \infty$. Under assumptions (ii) and (iii), lemma 2 shows that the left hand side of Eq. (4.4) and the terms (4.4a) and (4.4c) are $o(1/\lambda^\gamma)$.

Therefore, one must have

$$z \int_{B(0,r)} dy\, \rho_{\alpha_1}(x_\lambda)[E^*(x_\lambda) - E(x_\lambda)] = o(1/\lambda^\gamma) . \qquad (4.5)$$

Moreover, assumption (ii) enables us to apply lemma 1 to find the asymptotic behavior of $E^*(x_\lambda) - E(x_\lambda)$:

$$E^*(x_\lambda) - E(x_\lambda) = G^* - G + \frac{\hat{u}}{\lambda^\gamma} \int_{\mathfrak{D}} dy [C^*(y) - C(y)] + o(1/\lambda^\gamma). \qquad (4.6)$$

Combining Eqs. (4.5) and (4.6) (using also the fact that the average local density of particles does not vanish), one gets

$$G^* - G + \frac{\hat{u}}{\lambda^\gamma} \int_{\mathfrak{D}} dy[C^*(y) - C(y)] = o(1/\lambda^\gamma) . \qquad (4.7)$$

When $\gamma > 0$, this implies $G^* = G$, the complete shielding property [Eq. (4.1)], and $E^*(x_\lambda) - E(x_\lambda) = o(1/\lambda^\gamma)$.

(1) In a one dimensional Coulomb system, $\gamma = \nu - 1 = 0$, and therefore Eq. (4.7) does not imply complete shielding.

(2) Assumption (ii) implies no more than the local excess of charge created by the introduction of the external charges is finite (i.e., $|\int_{\mathfrak{D}} dy[C^*(y) - c(y)]| < \infty$). Then, the fact that complete shielding occurs (i.e., $\int_{\mathfrak{D}} dy[C^*(y) - C(y)] = 0$) is really a consequence of the equilibrium and clustering properties of the state. It is the clustering property which fails in two dimensions at low temperatures.[19]

*Note added in proof*: B. Jancovici (private communication) has recently found that for the semi-infinite jellium system in two dimensions, at the special temperature $(z^2/k_B T) = 2$, the truncated pair correlation decays, in the direction parallel to the wall, only as $r^{-2}$. In all other directions it decays like a Gaussian. Our clustering conditions are therefore not satisfied. He finds that the $l=0$ sum rule is satisfied, but not the $l = 1, 2$. It is not clear just how general this slow decay may be, but it certainly argues for caution in assuming exponential screening, in the manner of Debye, even at high temperatures. [c.f. also, B. Jancovici, Phys. Rev. Lett. 46, 386 (1981).]

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## APPENDIX A

We consider thermodynamic limits of globally neutral states confined between two plane electrodes. The finite volume system is defined by a cube $\Lambda$ of linear dimension $L$ with the electrodes perpendicular to the axis $e_1 = (1, 0, 0)$. The electrodes carry a uniform surface charge density $\pm C^{\text{wall}}$ at the right and left walls, giving rise to a constant external field $D = \omega_\nu C^{\text{wall}} e_1 (\omega_1 = 2,$ $\omega_2 = 2\pi,\ \omega_3 = 4\pi)$. We use periodic boundary conditions in the other directions.

One has $E^\Lambda(x) = D$ when $x$ is located on one of the electrodes. We investigate the following two situations:

(a) the infinite state with $\mathfrak{D} = \mathbf{R}^\nu$ obtained by removing both electrodes to infinity,

(b) the semi-infinite state with $\mathfrak{D} = \mathbf{R}^\nu_+ = \{x \in \mathbf{R}^\nu;$ $x^1 \geq 0\}$ obtained by removing the right electrode to infinity.

We argue first that the effective field is constant in both situations. By symmetry, the charge density depends only on the component $x^1$ of $x$. Therefore, integrating the Coulomb force $x/|x|^\nu$ in the 2–3 plane in Eq. (1.7) gives

$$G^{(a)}(x) = D + \lim_{L\to\infty} \frac{e_1\omega_\nu}{2} \int_{-L/2}^{L/2} \operatorname{sign}(x' - y')[C^\Lambda(y') - C(y')]dy' \qquad (A1)$$

in case (a) and

$$G^{(b)}(x) = D + \lim_{L\to\infty} \frac{e_1\omega_\nu}{2} \int_0^L \operatorname{sign}(x' - y')[C^\Lambda(y') - C(y')]dy' \qquad (A2)$$

in case (b).

Let us assume that $C^\Lambda(y)$ converges to its bulk value in such a way that

$$|C^\Lambda(y') - C(y')| \leq g[d(y, \partial\Lambda)] ,$$

where $d(y, \partial\Lambda)$ is the distance of $y$ to the boundary electrode and $g(x)$ an integrable function. Then it is easy to check that the limits in Eqs. (A1) and (A2) exist and are independent of $x$. In both cases $G(x) = G$ is simply related to the average polarization.

The average polarization

$$\overline{P}=\lim_{\Lambda\to\mathfrak{D}}\frac{1}{|\Lambda|}\int_\Lambda x\,C^\Lambda(x)\,dx$$

is linked to the average field

$$\overline{E}=\lim_{\Lambda\to\mathfrak{D}}\frac{1}{|\Lambda|}\int_\Lambda E^\Lambda(x)\,dx$$

by the usual formula

$$D=\overline{E}+\omega_\nu\overline{P}\ . \tag{A3}$$

Assuming that the infinite state in case (a) is translation invariant and locally neutral, e.g., $E(x)=E=E$ and $C(x)=0$, we have from Eqs. (1.6) and (A3),

$$G^{(a)}=\overline{E}=D-\omega_\nu\overline{P}\ . \tag{A4}$$

In the second case, the state will be invariant under translations perpendicular to $e_1$ and the charge density will thus depend only on $x_1$. It will presumably be different from zero only in the neighborhood of $x_1=0$. Equation (1.6) gives

$$E(x')=G^{(b)}+\frac{e_1\omega_\nu}{2}\int_0^\infty \operatorname{sign}(x'-y')C(y')\,dy'\ . \tag{A5}$$

As $x'\to\infty$, $E(x')$ converges to its bulk value $E$ whereas $E(x'=0)=D$.

This implies

$$\overline{E}=E=G^{(b)}+\frac{e_1\omega_\nu}{2}\int_0^\infty dy'C(y')\ , \tag{A6}$$

$$D=G^{(b)}-\frac{e_1\omega_\nu}{2}\int_0^\infty dy'\,C(y')\ , \tag{A7}$$

i.e.,

$$\overline{E}=e_1\omega_\nu\left[C^{\text{wall}}+\int_0^\infty dy'\,C(y')\right]\ .$$

We conclude now from Eqs. (A3), (A6), and (A7) that

$$\overline{P}=-e_1\int_0^\infty dy'\,C(y')$$

and

$$G^{(b)}=D-\tfrac{1}{2}\omega_\nu\overline{P}\ .$$

Finally, let us note that the complete shielding of the electrode (which is true at high temperatures for $\nu=2$ and is expected always in three dimensions), i.e.,

$$C^{\text{wall}}+\int_0^\infty dy'\,C(y')=0\ ,$$

is equivalent to the vanishing of the bulk electric field, i.e., $E=0$. Therefore, $G^{(a)}=0$ in case (a), but $G^{(b)}=\frac{1}{2}\omega_\nu\overline{P}=-\frac{1}{2}e_1\,\omega_\nu\,C^{\text{wall}}\neq 0$ in case (b).

## APPENDIX B

In Sec. III, we have derived the $l$-sum rules connecting the one and two point correlation functions. Following exactly the same arguments, one can derive the sum rules (2.1a), (2.2a), and (2.3a), connecting the $n$ and $(n+1)$ point functions. Let the asymptotic behavior of the force be characterized by conditions (F1) and (F2). The needed clustering conditions for the higher order correlation functions are

$$\rho(q_1Q)-\rho(q_1)\rho(Q)=O(1/|x_1|^{\nu+l+\epsilon})\quad(\epsilon>0)\ , \tag{B1}$$

uniformly with respect to $x_2$ when $n\geq 3$, where we have written $Q=(q_2\cdots q_n)$, $n\geq 2$.

Then the sum rules (2.1a), (2.2a), and (2.3a) follow when Eq. (B1) holds with $l=0, 1,$ and $2$, respectively.

## APPENDIX C

### Lemma 1

Let $F(x)$ be a locally integrable function on $\mathbf{R}^\nu$, and continuously differentiable up to order $(l+1)$ in a neighborhood of $x=\infty$ with

(i)

$$\lim_{\lambda\to\infty}\lambda^{\gamma+k}(\partial^{(k)}_{i_1\cdots i_k}F)(\lambda\hat{u})=d_{i_1\cdots i_k}(\hat{u}),\quad |\hat{u}|=1,\quad k=0,\ 1,\ \ldots,\ l\ ,$$

(ii)

$$(\partial^{(l+1)}_{i_1\cdots i_l}F)(x)=o(1/|x|^{\gamma+l}),\quad |x|\to\infty\ .$$

Consider a locally integrable function $g(x)$ on a domain $\mathfrak{D}$ in $\mathbf{R}^\nu$ with

(iii)

$$g(x)=O(1/|x|^{\nu+l+\epsilon})\quad(\epsilon>0)$$

for $x\to\infty$ in $\mathfrak{D}$.

Set

$$x_\lambda=\lambda\hat{u}+y,\quad \hat{u},\quad y\in\mathbf{R}^\nu,\quad |\hat{u}|=\lambda\ .$$

Then for any fixed $\hat{u}$, $y$,

$$\lim_{\lambda\to\infty}\lambda^{\gamma+l}\int_{\mathfrak{D}}\left[F(x_\lambda-x)-\sum_{m=0}^{l-1}\frac{(-1)^m}{m!}(\partial^{(m)}_{i_1\cdots i_m}F)(x_\lambda)x^{i_1}\ldots x^{i_m}\right]\times g(x)\,dx=\frac{(-1)^l}{l!}d_{i_1\cdots i_l}(\hat{u})\int_{\mathfrak{D}}x^{i_1}\ldots x^{i_l}g(x)\,dx,$$

uniformly with respect to $y$ in compact sets.

### Proof

We remark that assumptions (i) and (ii) imply

$$(\partial^{(k)}_{i_1\cdots i_k}F)(x)=O(1/|x|^{\nu+k}),\quad |x|\to\infty,\quad k=0,\ 1,\ \ldots,\ l \tag{C1}$$

and

$$\lim_{\lambda\to\infty}\lambda^{\gamma+l}(\partial^{(l)}_{i_1\cdots i_l}F)(x_\lambda)=d_{i_1\cdots i_l}(\hat{u})\ . \tag{C2}$$

Let $R_k(x_\lambda,x)$ be the rest of the Taylor expansion up to order $k$ of $F(x_\lambda-x)$ around $x_\lambda$, i.e.,

$$R_k(x_\lambda,x)=F(x_\lambda-x)-\sum_{m=0}^{k}(-1)^m\frac{1}{m!}x^{i_1}\ldots x^{i_m}(\partial^{(m)}_{i_1\cdots i_m}F)(x_\lambda). \tag{C3}$$

With this definition and Eq. (C2) the statement of the lemma is thus equivalent to

$$\lim_{\lambda\to\infty}\lambda^{\gamma+l}\int R_l(x_\lambda,x)g(x)\,dx=0\ . \tag{C4}$$

In order to prove Eq. (C4), we divide the domain $\mathfrak{D}$ into four pieces. Fix a number $r$ such that Eq. (C1) holds for $|x|\geq r$, and then choose $\lambda$ such that $|x_\lambda|>r$ and Eq. (C1) and (ii) and (iii) hold for $|x|\geq\frac{1}{2}|x_\lambda|-r$; then we define

$$\mathfrak{D}^1_\lambda=\{x\in\mathfrak{D};\ \ |x|\leq\tfrac{1}{2}|x_\lambda|\}\ ,$$

$$\mathfrak{D}^2_\lambda=\{x\in\mathfrak{D};\ \ |x|\geq\tfrac{3}{2}|x_\lambda|\}\ ,$$

$$\mathfrak{D}^3_\lambda=\{x\in\mathfrak{D};\ \ |x_\lambda-x|<r\}\ ,$$

$$\mathfrak{D}^4_\lambda=\{x\in\mathfrak{D};\ \ \tfrac{1}{2}|x_\lambda|<x<\tfrac{3}{2}|x_\lambda|,\ \ |x_\lambda-x|\geq r\}\ ,$$

and denote the corresponding integrals by

$$I^j_\lambda=\lambda^{\gamma+l}\int_{\mathfrak{D}^j_\lambda}R_l(x_\lambda,x)g(x)\,dx,\quad j=1,\ \ldots,\ 4\ .$$

In $\mathfrak{D}_\lambda^1$, we use the estimate on the rest of the Taylor expansion

$$|R_k(x_\lambda,x)| \le c_k |x|^{k+1} \sup_{\substack{l_1+\cdots+l_\nu=k+1\\ l_i\ge 0}} \; \sup_{0\le\vartheta\le 1} \times \left| \frac{\partial^{(k+1)}}{\partial x_1^{l_1}\cdots\partial x_\nu^{l_\nu}} F(x_\lambda-\vartheta x)\right| \qquad \text{(C5)}$$

together with the fact that

$$|x_\lambda - \vartheta x| \ge |x_\lambda| - |x| \ge \tfrac{1}{2}|x_\lambda|$$

to obtain from Eq. (C1)

$$R_{l-1}(x_\lambda,x) = |x|^l\, O(1/|x_\lambda|^{\gamma+l}) = |x|^l\, O(1/\lambda^{\gamma+l})$$

and

$$R_l(x_\lambda,x)=R_{l-1}(x_\lambda,x) - \frac{(-1)^l}{l!} x^{i_1}\cdots x^{i_l}(\partial^{(l)}_{i_1\cdots i_l}F)(x_\lambda) = |x|^l\, O(1/\lambda^{\gamma+l}) \,. \qquad \text{(C6)}$$

Therefore, Eq. (C6) and (iii) show that

$$\lambda^{\gamma+l} R_l(x_\lambda,x)g(x) = o[|x|^l g(x)]$$

is majorized uniformly in $\lambda$ by an integrable function of $x$.

Moreover, we get also from Eq. (C5) and assumption (ii),

$$R_l(x_\lambda,x)=|x|^{l+1}\, o(1/\lambda^{\gamma+l}) \,,$$

i.e.,

$$\lim_{\lambda\to\infty}\lambda^{\gamma+l}R_l(x_\lambda,x)g(x)=0 \,.$$

Thus, $\lim_{\lambda\to\infty} I_\lambda^1=0$ follows by dominated convergence.

In $\mathfrak{D}_\lambda^2$ we have $|x|\ge\frac{3}{2}|x_\lambda|$, $|x_\lambda - x|\ge\frac{1}{2}|x_\lambda|$. We get from Eq. (C1)

$$F(x_\lambda-x)=O(1/|x_\lambda|^\gamma)=|x|^l\, O(1/\lambda^{\gamma+l}) \,,$$

$$x^{i_1}\cdots x^{i_m}(\partial^{(m)}_{i_1\cdots i_m}F)(x_\lambda)=|x|^m\, O(1/|x_\lambda|^{\gamma+m})$$

$$= |x|^l\, O(1/\lambda^{\gamma+l}), \quad m=0,\, 1,\, \ldots,\, l \,,$$

and thus

$$R_l(x_\lambda,x)=|x|^l\, O(1/\lambda^{\gamma+l}) \,.$$

Therefore, $I_\lambda^2=O[\int_{\mathfrak{D}_\lambda^2}|x|^l g(x)]$ tends to zero as $\lambda\to\infty$ since $|x|^l g(x)$ is integrable on $\mathfrak{D}$.

In both $\mathfrak{D}^3_\lambda$ and $\mathfrak{D}^4_\lambda$ we have $|x_\lambda/2|\le|x|\le\frac{3}{2}|x_\lambda|$. We get then from Eq. (C1) and (iii),

$$x^{i_1}\cdots x^{i_m}(\partial^{(m)}_{i_1\cdots i_m}F)(x_\lambda)=|x|^m\, O(1/|x_\lambda|^{\gamma+m}) = O(1/\lambda^\gamma) \,,$$

$$g(x)=O(1/|x_\lambda|^{\nu+l+\epsilon})=O(1/\lambda^{\nu+l+\epsilon}) \,.$$

This implies

$$R_l(x_\lambda,x)=F(x_\lambda-x)+O(1/\lambda^\gamma) \,.$$

Therefore, if $x\in\mathfrak{D}^3_\lambda$, $|x_\lambda-x|\le r$, and one has

$$I^3_\lambda = O\left(\frac{1}{\lambda^{\nu-\gamma+\epsilon}}\right)\int_{|x_\lambda-x|<r} dx\,|F(x_\lambda-x)| + O\left(\frac{1}{\lambda^{\nu+\epsilon}}\right) \,.$$

By the local integrability of $F(x)$,

$$\int_{|x_\lambda-x|\le r} dx\,|F(x_\lambda-x)|=\int_{|y|\le r}dy\,|F(y)|<\infty$$

and hence

$$\lim_{\lambda\to\infty} I^3_\lambda=0 \,.$$

If $x\in\mathfrak{D}^4_\lambda$ we have now $|x_\lambda-x|\ge r$, implying

$$R_l(x_\lambda,x)=O(1/|x_\lambda-x|^\lambda)+O(1/\lambda^\gamma)$$

and therefore

$$I^4_\lambda = O\left(\frac{1}{\lambda^{\nu-\gamma+\epsilon}}\right)\int_{\mathfrak{D}^4_\lambda}\frac{dx}{|x_\lambda-x|^\gamma}+O\left(\frac{1}{\lambda^{\nu+\epsilon}}\right)\int_{\mathfrak{D}^4_\lambda}dx \,.$$

An estimate of potential theory gives[20]

$$\int_{\mathfrak{D}^4_\lambda} dx\, \frac{1}{|x_\lambda-x|^\gamma} = \begin{cases} O(\rho^{\nu-\gamma}), & \gamma<\nu \,, \\ O(\ln\rho), & \gamma=\nu \,, \end{cases}$$

where $\rho$ is the radius of a ball of volume equal to that of $|\mathfrak{D}^4_\lambda|$. Since the latter volume is $O(\lambda^\nu)$, we get

$$\int_{\mathfrak{D}^4_\lambda} dx\, \frac{1}{|x_\lambda-x|^\gamma} = \begin{cases} O(\lambda^{\nu-\gamma}), & \gamma<\nu \,, \\ O(\ln\lambda), & \gamma=\nu \,. \end{cases}$$

With this one finds

$$I^4_\lambda = \begin{cases} O(1/\lambda^\epsilon), & \gamma<\nu \,, \\ O(\ln\lambda/\lambda^\epsilon), & \gamma=\nu \,, \end{cases}$$

which tends to zero as $\lambda\to\infty$.

This concludes the proof of the lemma.

### Lemma 2

Integrating the left-hand side of Eq. (2.5) on a sphere of radius $r$ centered in $\lambda\hat{u}$ and transforming the volume integral into a surface integral gives rise to the term

$$k_BT\int_{B(0,r)}\nabla_{x_1}\rho^T_{\alpha_1\alpha_2}(\lambda\hat{u}+y,x_2)$$

$$= k_BT\int_{\partial B(0,r)}\rho^T_{\alpha_1\alpha_2}(\lambda\hat{u}+y,x_2)$$

$$= k_BT\,|\partial B(0,r)|\,o(1/\lambda^{\gamma+l})$$

by virtue of the clustering assumption (C1).

The boundedness of the effective field and of $F^w(q)$ away from the boundary of $\mathfrak{D}$ insures that the term (2.5a) is also $O(1/\lambda^{\gamma+l})$.

We write the term (2.5c), i.e.,

$$\lambda^{\gamma+l}\int_{\mathfrak{D}} dx\, F(x_\lambda-x)\sum_\alpha z_\alpha\rho^T_{\alpha_1\alpha_2\alpha}(x_\lambda,x_2,x) \,,$$

as a sum of integrals over $\mathfrak{D}^i_\lambda$, $i=1,\, 2,\, 3,\, 4$.

The clustering assumption (C2) of Sec. II implies that

$$g_\lambda(x)=\sum_\alpha z_\alpha\rho^T_{\alpha_1\alpha_2\alpha}(x_\lambda,x_2,x)$$

satisfies condition (iii) of lemma 1 uniformly with respect to $\lambda$. Then it follows exactly as in lemma 1 that the integrals on $\mathfrak{D}^i_\lambda$, $1=2,\, 3,\, 4$ tend to zero as $\lambda\to\infty$. Using condition (C2) again, we are left with

$$\lambda^{\gamma+l}\int_{|x|\le\lambda/2} dx\, F(x_\lambda-x)\left|\sum_\alpha z_\alpha\rho^T_{\alpha_1\alpha_2\alpha}(x_\lambda,x_2,x)\right|$$

$$= \lambda^{\gamma+l}\,O\left(\frac{1}{\lambda^{\nu+l+\epsilon}}\right)\int_{|x|\le\lambda/2} dx\, \frac{1}{|x_\lambda-x|^\gamma} = O\,\frac{1}{\lambda^\epsilon}\to 0, \quad \lambda\to\infty.$$

The left-hand side of Eq. (4.4) and the terms (4.4a) and (4.4c) are estimated in a similar way.

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